DEFINING THE OPERATING CONDITIONS OF THE ATTRITION-LEACHING PROCESS USING THERMODYNAMIC PROCESS MODELLING

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ABSTRACT

The attrition-leaching process aims at improving leaching performance when formation of passivation layers at the surface of leached particles is a severe limiting factor, as discussed recently by Julcour and coworkers (Julcour et al., 2015). This paper proposes a geochemistry-based modelling scheme for deriving the window of possible operating conditions for the attrition-leaching process to match the properties of the processed ore. The rationale is that the attrition-leaching process maintains the surface of reacting particles in an unpassivated state by continuous mechanical removal of surface leach layers, so that the process reactions can be modelled from thermodynamic equilibria throughout the duration of the process. The strength of the proposed modelling approach is that it bridges the gap between the properties of the ore and the process operating conditions. The present paper exemplifies the proposed process modelling route for derivation of the attrition-leaching process operating conditions in the context of the leaching of silicate ores, matching model predictions against controlled laboratory experiments. It is shown how thermodynamic modelling, when used in conjunction with a solid knowledge of the phases present in the system, can assist with deciding upon suitable process operating conditions. As an example, this first-principle modelling approach predicted that steel grinding medium would be converted into siderite ($FeCO_3$) under a wide range of operating conditions, which led to questioning this initial choice of grinding medium for the attrition-leaching process under mineral carbonation conditions. It is emphasised that the same approach could be applied to ores of greater economic significance.

KEYWORDS

Attrition-leaching process, thermodynamic process modelling, mineral carbonation

INTRODUCTION

The attrition-leaching process is remarkable in that, by principle, it maintains the surface of reacting particles in an unpassivated state by continuous mechanical removal of surface leach layers. Despite the value of this process having been recognised as early as 1981 (Kawabata, 1981; Evans and Liddell, 1991), it has surprisingly not led to any industrial development. The reason for the absence of industrial follow-up of this process is unclear, particularly in light of some very attractive features. One such feature is that the attrition-leaching can be performed inside stirred mills, whose scalability and industrial performance are beyond questioning.

From a modelling perspective, which is at the core of the present paper, the attrition-leaching process is particularly interesting. Indeed, as the particle surface composition remains unchanged throughout the process due to the continual removal of passivation layers, our belief is that such process is only driven by dissolution kinetics of fresh surfaces and thermodynamic equilibria. As a result, it should be possible to model the performance of any attrition-leaching process from first principles at the local scale, such that thermodynamic modelling can be used to determine the likely window of operating conditions, which is an immense challenge from experiments alone. This modelling capability, which flows directly from the unique nature of the process, permits bridging the gap between the properties of the ore and the process operating conditions.

The illustrative example presented here is that of the leaching of Mg and Fe cations from silicate ores, for the sake of mitigating CO_2 emissions by ex-situ mineral carbonation. Although leaching of silicate ores is not a significant topic in the minerals industry, it is a sensible example in the context of this paper as silicate ores are not easily leachable, and prone to forming complex surface layers that impede the leaching process (Bonfils et al., 2012). Moreover, choosing the mineral carbonation process as this paper's illustrative example is quite pertinent given its intrinsic complexity. Firstly, this process mixes a number of concomitant processes, which include leaching of silicate ores and precipitation of carbonates. Secondly, as it typically operates under a CO_2 partial pressure of 20 bar and a temperature of 180°C, the mineral carbonation process is characterised by a complex reactive system; this yields a convincing case study for demonstrating the value of thermodynamic process modelling as a decision-making tool for choosing suitable operating conditions of the attrition-leaching process.

The overall method applied here consists in coupling thermodynamic calculations and, to a lesser extent, kinetic models to the mineral carbonation process. Calculations are matched against experimental results in order to demonstrate that thermodynamic equilibrium is reached, which illustrates the relevance of the proposed modelling approach. After a short description of both the experimental and modelling techniques, three case studies are presented.

EXPERIMENTAL

A brief description of the experimental device and procedures are provided in this section. All details are provided in Julcour et al. (2015).

Experimental Device

A 300 mL stirred autoclave reactor was modified and used as a high pressure high temperature stirred bead mill. The set-up permits conducting direct aqueous mineral carbonation experiments in batch mode, under controlled temperature and pressure conditions, with concomitant attrition. The CO_2 pressure inside the reactor is regulated using a CO_2 ballast tank and gas pressure regulator, and instantaneous CO_2 consumption by the liquid–solid suspension is monitored by recording temperature and pressure inside the ballast. Slurry temperature is monitored and PID controlled.

The mechanical stirrer is rotated at moderate speed (800 rpm) to promote surface attrition of reactive particles. Dispersion of CO_2 is achieved by feeding the gas through the stirrer hollow tubing for efficient gas–liquid mass transfer. A glass jacket is used to prevent reactor wear.

Experimental Conditions

Minerals

The first mineral investigated, further referred to as KNS, is a by-product of the hydrometallurgical processing of nickel ore (Koniambo Nickel SAS, New Caledonia). It is collected from slags slowly cooled under ambient conditions. This fully crystallized material mainly consists in protoenstatite, clinoenstatite and forsterite phases. Its composition (wt. %) is as follow: SiO_2 52.1, MgO 28.8, Fe_2O_3 14.4, Al_2O_3 1.9.

The second one is a synthetic olivine from Magnolithe GmbH (Austria). This model material, produced by high temperature processing of natural dunite, mainly consists in forsterite. Its composition varies between $(Mg_{1.88}Fe_{0.12})SiO_4$ and $(Mg_{1.82}Fe_{0.18})SiO_4$ (Bodénan et al., 2014).

Before the carbonation tests, these solids were ground below 100 µm in order to yield measurable conversion within the considered reaction time (24 h).

Grinding Media

Two grinding media are used: 1.3 mm diameter alumina beads and 1.6 mm diameter stainless steel (AISI 420C) beads. A fixed volume of grinding beads (~ 80 mL) is introduced in the reactor.

Operating Parameters

The maximal CO_2 partial pressure (P_{CO2}) is fixed at 20 bar, which correspond to a total pressure ($P_{tot}=P_{CO2}+P_{H2O}$) of about 28 bar at 180°C. The operating temperature is in the range 40 to 180°C. A fixed mass of mineral (7.2 g) is introduced in 80 mL of ultra-pure water, leading to a concentration of 90 g/L of water.

Characterization of Solid Products

At the end of the reaction, the reactor internals are thoroughly cleaned with osmosed water to recover stuck solid particles. The resulting slurry is passed through a 0.2 µm micropore filter. The solid is then oven dried at 70 °C during 24 h before weighing and analysis by standard analytical techniques: XRD, ICP-AES (after acid dissolution), CHNS elemental analyser.

PROCESS MODELLING

Thermodynamic Modelling

The PHREEQC software, designed to perform a wide variety of aqueous geochemical calculations (Parkhurst and Appelo, 2013), was used to determine the thermodynamic equilibria in various conditions (T, gas composition and pressure, mineral composition). From an initial set of composition and conditions, this software computes the system equilibrium and outputs the amount and composition of the products (gas, liquid, solids), including the speciation of the aqueous phase.

We considered the initial following phases in order to represent the system contained in the batch reactor: a fixed volume (30 mL) gas phase; a liquid aqueous phase (80 mL); solid phases accounting for the processed mineral and the grinding media.

All simulations used the llnl.dat database based on the thermo.com.V8.R6.230 dataset prepared at the Lawrence Livermore National Laboratory (LLNL). The selection of this database followed a careful check of the equilibria related to the main components of the system, based on preliminary calculations and comparison with published experimental data. For instance, we verified that magnesite ($MgCO_3$) and siderite ($FeCO_3$) solubility in water were satisfactorily reproduced with respect to recent data presented by Bénézeth et al. (2011) and Fosbøl et al. (2010), respectively. The activity coefficients in the aqueous phase are calculated according to the LLNL aqueous model, which is a variant of the Debye-Hückel model (the so-called B-dot equation). This approach is justified by the low ionic concentration of our solutions (ionic strength of about 10^{-3} to 10^{-2}).

On top of the standard LLNL database, two kinds of data were included in the calculations. Firstly, we introduced Peng-Robinson parameters for the main gaseous compounds CO_2 and H_2O, in order to reproduce non-ideal behaviour of the gas phase, as recommended for high pressure gas mixtures. The Peng-Robinson model gives good prediction of experimental CO_2 solubility data in the aqueous phase (Nighswander et al. (1989), Zawisza and Malesinska (1981)) as well as pH values (Peng et al., 2013) in the CO_2-H_2O system for temperature up to 200°C and pressure up to 30 bar. Secondly, as recommended by Krupka, Cantrell and McGrail (2010), a number of solid solutions were taken into account in the equilibrium calculations. The $(Mg,Fe)CO_3$ solid solution was modeled with a regular solution parameter of 4.44 kJ/mol (Chai and Navrostki, 1996). The fcc (Fe,Cr) metal phase and the $(Fe,Mg)Cr_2O_4$ spinel phase were modelled as ideal regular solutions.

Kinetic Modelling

A kinetic model was combined with the thermodynamic equilibrium calculations with the aim of calculating reaction rates, thanks to the PHREEQC software. As a first assumption, we considered that the limiting step of the process was the dissolution of the initial mineral: precipitation of the solid products, dissolution of CO_2(g) in water and transport phenomena in solid and liquid phases were not taken into account in the kinetic model, assuming that thermodynamic equilibrium was reached at each time step. Furthermore, particle breakage and its impact on leaching was neglected in the modelling.

The dissolution of solid particles was modeled through a shrinking particle model which used a dissolution rate law established for fresh ore surface, with two main inputs (for more details, see Bonfils et al., 2012). The first input is the particle size distribution of the processed mineral. In the present model, the particle size distribution is divided into 22 size classes, whose contributions were calculated so as to mimic the measured particle size distribution. The second input is a set of three constants (k_0, E_a, n) that depends on the dissolving phase. These constants are used to determine the dissolution rate of the mineral. Considering the acidic conditions encountered in our aqueous solution, the surface reaction rate r (in $mol.m^{-2}.s^{-1}$) can be expressed according to Equation 1 (Palandri and Kharaka, 2004).

$$r = k_0.\exp(-E_a/RT).a_{(H+)}^{n} (1-10^{SI}) \quad (1)$$

where k_0 is the pre-exponential factor, E_a the activation energy, R the gas constant, T the absolute temperature, $a_{(H+)}$ the activity of the proton, n the reaction order of the proton, and SI the saturation index (=log (IAP/K_{SP}), with IAP the ion activity product and K_{SP} the solubility product of the mineral).

The overall lixiviation rate is then obtained as the product of r by the total surface of the particles.

CASE STUDY 1: DEFINING THE OPERATING CONDITIONS BEST SUITED TO THE MINERAL CARBONATION PROCESS

This case deals with the carbonation of the KNS mineral in the attrition-leaching reactor. The best suited condition range (T, P_{CO2}) based on thermodynamics and some basic kinetics considerations in the system ore+H_2O+CO_2 are discussed. The equilibrium of the system was first calculated for various T and P_{CO2}, considering that the grinding media had no influence on the chemical reactions. The carbonation

yield (R), which is a key process performance indicator, is defined here as the total amount (in moles) of iron and magnesium in carbonate phases divided by their initial amount in KNS. The ore was considered as an assemblage of 0.054 mol $MgSiO_3$ and 0.013 mol of $FeSiO_3$. At first, the most stable phases were allowed to form, with, in particular, quartz as the most stable phase for SiO_2.

For CO_2 partial pressures in the range 1 to 30 bar, equilibrium calculations revealed four distinct mineral speciation domains separated by three characteristic temperatures (T_1, T_2, T_3). The three temperatures were found to vary with P_{CO2}. This mineral speciation is summarized in Figure **1**, along with the mineral carbonation yield.

With the view of maximizing the formation of carbonates, thermodynamic modelling clearly shows that the operating temperature of the attrition-leaching process must be maintained below T_1: in this case, the model predicts that all Fe and Mg from the initial ore are converted into a carbonate solid solution (Mg, Fe)CO_3. At higher temperatures, both Fe and Mg form non carbonate phases like talc ($Mg_3Si_4O_{10}(OH)_2$) at $T>T_1$, magnetite (Fe_3O_4) at $T>T_2$ and antigorite ($Mg_{48}Si_{34}O_{85}(OH)_{62}$) at $T>T_3$.

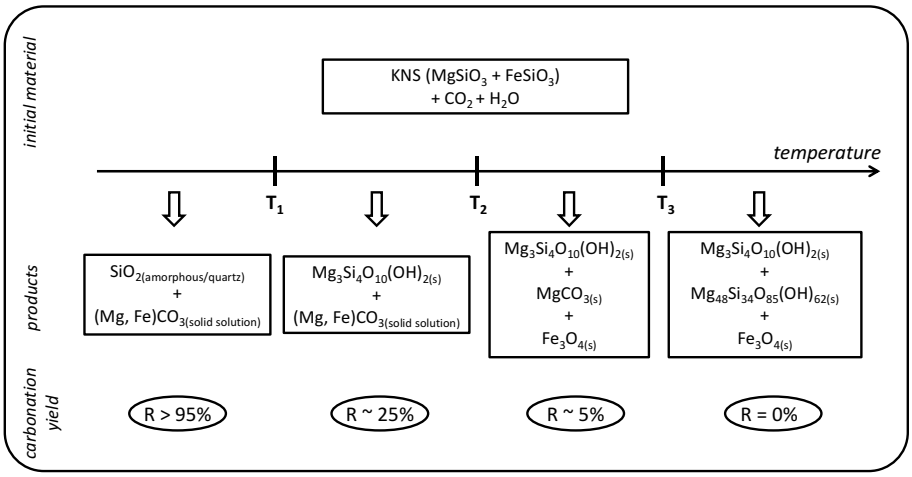

Figure 1 – Evolution of phase assemblage and carbonation yield (R) with temperature in the system $KNS+H_2O+CO_2$ at equilibrium, for $1<P_{CO2}<30$ bar

Figure 2 shows the values of T_1, T_2 and T_3 as well as the phase speciation for $P_{CO2}=10$ bar. These calculations illustrate that, above T_1, most of the magnesium is stabilised within the talc phase, which reduces considerably the carbonation yield. This example shows the value of thermodynamic modelling for setting the best operating conditions for the attrition-leaching process.

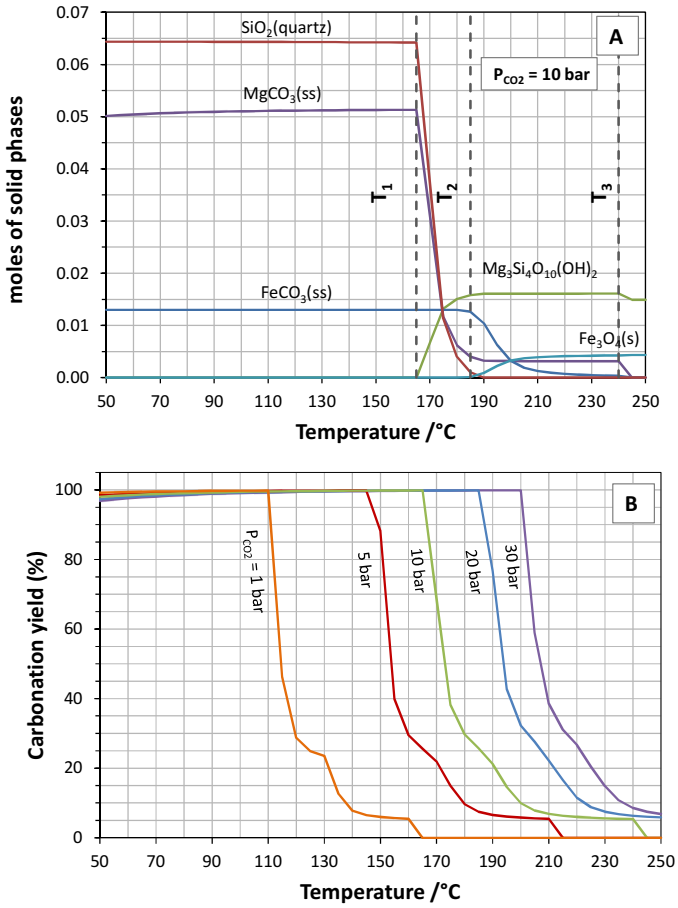

Figure 2 – Influence of temperature on the evolution of the mineral speciation (A) and carbonation yield (B) for the system KNS-CO_2-H_2O at equilibrium, considering $SiO_{2(quartz)}$ as stable silica phase

Figure **3** provides a closer look at the carbonation yield in the $50<T<T_1$ temperature range for P_{CO2}=20 bar, together with the concentration of the main elements in the aqueous solution. It shows that the total concentration of both Mg(+II) and Fe(+II) decreases with temperature, due to a stabilisation of the carbonate solid phase. In order to maximize the carbonation yield, a temperature as close as possible to T_1 is thus recommended by the model. This finer level of analysis of thermodynamic modelling results exemplifies the strength of the thermodynamic modelling approach for setting the operating conditions of the attrition-leaching process.

On top of this purely thermodynamic approach, additional considerations related to process kinetics provide additional guidance for choosing the best attrition-leaching process operating conditions.

First of all, although quartz is the most stable allotrope of silica in the operating conditions range, it has been shown that amorphous silica, not quartz, is likely to form by precipitation of dissolved silicon (Daval et al., 2011). Considering amorphous silica as the stable phase instead of quartz does not modify the mineral speciation reported in Figure **1**, but it has a major influence on the value of T_1. Indeed, for a given P_{CO2}, thermodynamic modelling (see Figure 4) predicts a decrease of T_1 of about 60 to 70°C compared to Figure **2** (B).

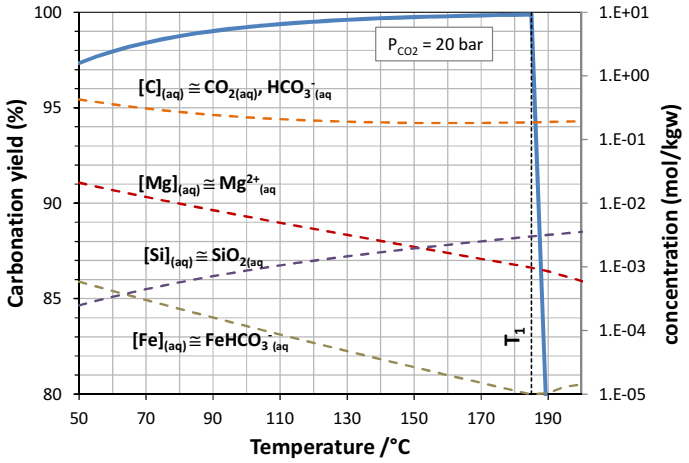

Figure 3 – Influence of temperature on carbonation yield and elements concentration (dashed lines) for the system KNS-CO_2-H_2O (P_{CO2}=20 bar) at equilibrium, considering $SiO_{2(quartz)}$ as the stable SiO_2 phase

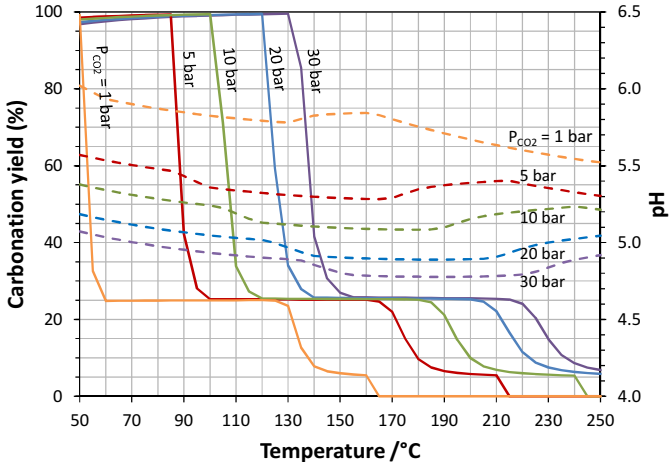

Figure 4 – Influence of temperature on carbonation yield and pH (dashed lines) for the system ore-CO_2-H_2O at equilibrium, considering $SiO_{2(amorphous)}$ as stable the stable SiO_2 phase

As for our experiments carried out with the KNS mineral, carbonation yields as high as 50% were obtained at P_{CO2} =20 bar and T=180°C, which could mean that quartz prevails on amorphous silica. However, no diffraction peak corresponding to quartz was evidenced by XRD analysis of the solid products. It is thus believed that other phyllosilicate compounds, not taken into account in the thermodynamic database, might form in addition to talc, or even replace it.

Secondly, experimental studies (e.g. Giammar et al., 2005) have shown that crystallisation of magnesite requires a temperature above 80°C. As a consequence, it can be read from Figure **4** that P_{CO2} should be at least equal to 5 bar, which sets yet another operating condition. This is an interesting result as standard attrition-leaching tests are typically run at a P_{CO2} of 20 bar, which represent more energy intensive conditions than those suggested by the model.

Finally, as detailed in Equation 1, standard kinetic dissolution models of silicate materials include a term related to the proton concentration, and as a consequence acid media are acknowledged to increase

their dissolution rate. As illustrated in Figure **4**, the proton concentration in the ore+H_2O+CO_2 system increases by almost one decade between P_{CO2} = 1 bar and P_{CO2} = 30 bar. High CO_2 partial pressures are thus required to promote the leaching of the mineral, and thus the overall carbonation reaction kinetics.

The explanation for the decrease in pH with increasing temperature lies in the speciation of the aqueous solution. Indeed, two main equilibria control the pH of the solution: an acid contribution from the dissolution of CO_2 (Equation 2) and an alkaline contribution from the dissolution of MgO contained in $MgSiO_3$ (Equation 3).

$$CO_{2(g)} + H_2O = HCO_3^-{}_{(aq)} + H^+{}_{(aq)} \quad (2)$$

$$MgO_{(KNS)} + H_2O = Mg^{2+}{}_{(aq)} + 2\ OH^-{}_{(aq)} \quad (3)$$

For a given P_{CO2}, pH is thus mostly dependent on the concentration of Mg^{2+} in the aqueous phase and consequently of the solid carbonate phase solubility. As evidenced in Figure **3**, the concentration of Mg^{2+} decreases with temperature, which promotes a decrease in pH.

As a first conclusion, thermodynamic modelling is shown to be a powerful decision-making tool for defining the operating conditions best suited to the mineral carbonation process. A high CO_2 partial pressure decreases pH and thus enhances the dissolution kinetics of the initial material. For a given P_{CO2}, a temperature as close as possible to the critical temperature T_1, which corresponds to the formation of talc, will maximize the carbonation yield. It is likely that an improvement of the thermodynamic database would allow to match more closely the prediction of the observed by-products and carbonation yields. This supports our conviction that a to-and-from between modelling and experimental data is required to describe such complex multi-element systems.

CASE STUDY 2: OF THE USE OF METAL BEADS AS GRINDING MEDIUM

The attrition-leaching process can be operated in different ways, i.e. with grinding medium, semi-autogenously or fully autogenously. Thermodynamic modelling, in the context of the mineral carbonation process, proved particularly insightful for choosing the grinding medium. The example that follows looks at the possibility of using steel or nickel-base beads as grinding medium in this particular context, with an interrogation as to whether the beads might affect the chemistry of the mineral carbonation process.

In order to evaluate the chemical influence of stainless steel used as grinding medium in the attrition-leaching reactor, an increasing amount of ($Fe_{0.87}Cr_{0.13}$) solid solution was added into the earlier ore+H_2O+CO_2 system. As shown in Figure **5**, for the set of conditions T=120°C and P_{CO2}=20 bar, at equilibrium, thermodynamic modelling predicted that the steel beads would be fully converted into siderite ($FeCO_3$) and chromite ($FeCr_2O_4$). As a consequence of Fe (and, to a minor extent, Cr) oxidation, it was also predicted that solid carbon would be produced according to the overall Equation 4.

$$Fe_{(steel)} + 3/2CO_{2(aq)} = FeCO_{3(ss)} + 1/2C_{(s)} \quad (4)$$

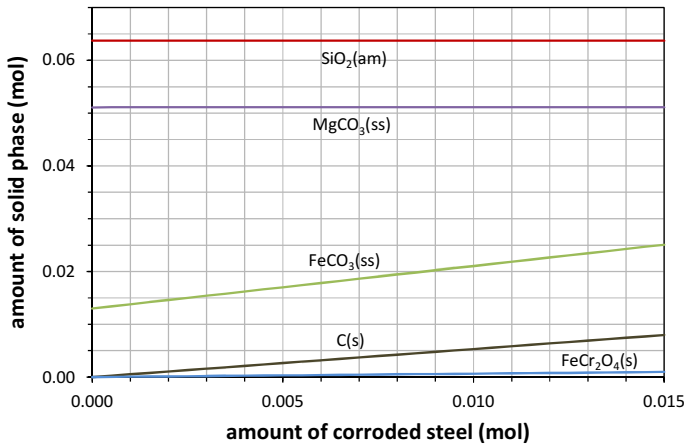

Figure 5 – Equilibrium in the system ore-CO_2-H_2O+steel at P_{CO2}=20 bar, T=120°C

Similar results were obtained in the $1<P_{CO2}<30$ bar, $T<T_1$ range. The practical consequence of this calculation is that stainless steel grinding balls are foreseen to be chemically unstable inside the attrition-leaching reactor under the operating conditions of the mineral carbonation process. Even if siderite (Fosbøl et al., 2010) and chromium-enrich films (Brooks et al., 1986) are usually considered as a passivating corrosion products of steel, in our specific case mechanical grinding is rather likely to peel off these phases, leading to a quantitative corrosion of the grinding beads.

Experimental tests operated with 1.6 mm stainless steel beads clearly confirmed the occurrence of the corrosion phenomenon predicted by thermodynamic modelling. Indeed, XRD analysis confirmed that, after a run of 24 hrs at T=120°C and P_{CO2} = 20 bar, iron in the final solid product is fully carbonated, either as pure siderite or as a $(Mg,Fe)CO_3$ solid solution. While the absence of corrosion products at the surface of the grinding beads was verified through microscopic observations, ICP-AES analysis of the solid product showed a significant increase of the Fe content. The molar ratio Fe/(Fe+Mg) in the initial ore is 0.20 compared to about 0.48 in the final product, accounting for an addition of 0.035 mol of elemental iron. This corresponds to a consumption of stainless steel beads of about 2.2 g. The corrosion phenomenon is thus relatively limited compared to the initial mass of beads (0.33 % of 675 g), and the corrosion rate of steel can be estimated around 0.3 mm/year. However, under the specific conditions of the batch reactor considered here, the total amount of iron carbonated during 24 h due to the beads corrosion is of the same order of magnitude as the total amount of ore being carbonated.

The combination of thermodynamic calculations and short duration experiments finally leads to the conclusion that stainless steel beads are not suited for the attrition-leaching process in the context of mineral carbonation of silicate ores. Similar calculations were carried out with nickel metal as a potential grinding medium, accounting for the whole range of Ni-base alloys that could withstand the prevailing acid aqueous conditions. However, similarly to iron, thermodynamic modelling predicted that nickel would oxidise in the range of operating conditions, its stable form being either $NiO_{(s)}$ or $NiSiO_{3(s)}$. Based on the experimental evidence obtained with stainless steel, it is most likely that carbonation operating conditions combined with the exfoliation of oxide layers would lead to quantitative corrosion of any Ni-base alloy grinding media.

Since the most common structural alloys (Fe and Ni-base) are foreseen to suffer from corrosion, thermodynamic modelling results lead to the conclusion that non-metallic grinding media must be used inside the attrition-leaching reactor in the context of mineral carbonation.

CASE STUDY 3: COUPLING KINETICS AND THERMODYNAMICS

The case of the carbonation of olivine using alumina beads is considered here, in the view of validating our main hypothesis, which is that thermodynamic equilibrium is reached in the attrition-leaching reactor. The main reason guiding the choice of this specific mineral is that many academic studies provide reliable dissolution kinetic parameters (k_0, E_a, n; see Equation 1) that are required to derive the thermodynamic model. We have chosen here the parameters from Prigiobbe et al. (2009) obtained in the H_2O-CO_2 system: $k_0 = 2640$ mol.m^{-2}.s^{-1}; $E_a = 52.9$ kJ.mol^{-1}; n = 0.52.

The input phase is 0.051 mol of forsterite Mg_2SiO_4. The particle size distribution used in the model is adjusted to the measured one (Figure **6**). The solid phase speciation at equilibrium is similar to the one presented in Figure **1**, considering the formation of quartz. As illustrated by Figure **7**, which provides the evolution of the carbonation yield as measured and calculated, a good agreement is reached between experimental data and modelling. The relevance of the overall modelling is thus validated. Indeed, for each time step related to the surface reaction of olivine, thermodynamic equilibrium is reached. This means that the reaction products do not stay at the surface of the mineral particles and that the reaction kinetics is driven by the dissolution of the mineral.

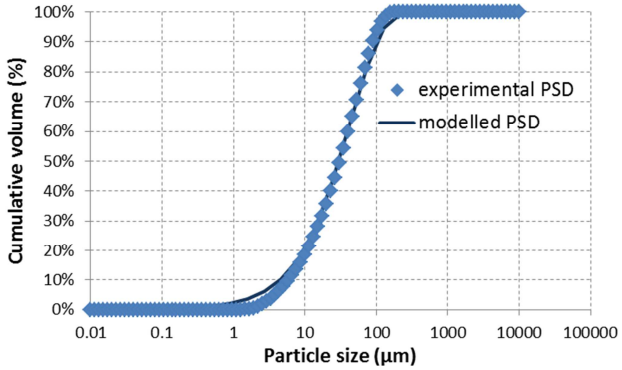

Figure 6 – Particle size distribution (PSD) of the olivine sample after grinding: measured and modelled cumulative volume versus particle size

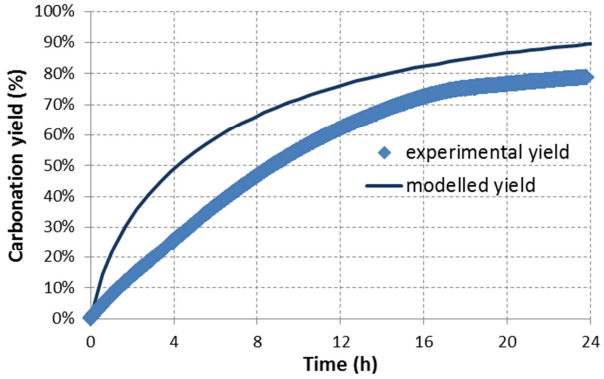

Figure 7– Comparison between experimental data and shrinking particle simulation (olivine mineral, T=180°C, P_{CO2}=20 bar)

CONCLUSIONS

The formation of passivating layers is a common feature of lixiviation process, leading to almost unpredictable performance owing to their variety and high sensitivity towards the reaction medium and operating conditions. It is shown that the proposed attrition-leaching process can continuously remove those passivating layers, thereby enabling the thermodynamic modelling to be a most valuable tool to define the operating window range for quantitative extraction yields. These calculations can also assist material selection for the process equipment as exemplified here for the grinding media. Nonetheless for complex systems such as those encountered in the carbonation of silicate ores, the existing databases need to be improved, in order to allow a more accurate thermodynamic description of phyllosilicate phases. The process dynamics is also well predicted by coupling thermodynamic calculations with chemical kinetics through the classical shrinking particle model, only accounting for the initial particle size distribution.

Future work will describe the concomitant breakage of the particles, whose effect is of special interest in the context of autogenous attrition - probably the most sober operating mode, where the reacting particles are used as grinding media. Attrition-leaching modelling of other minerals of great economical impact, such as chalcopyrite, will also be addressed.

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